

## *Programma comune*



## PC-01      **TiO<sub>2</sub> Photocatalysis and Related Surface Phenomena**

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The field of photocatalysis can be traced back more than 80 years to early observations of the chalking of titania-based paints and to studies of the darkening of metal oxides in contact with organic compounds in sunlight. During the past 20 years, it has become an extremely well researched field due to practical interest in air and water remediation, self-cleaning surfaces, and self-sterilizing surfaces. During the same period, there has also been a strong effort to use photocatalysis for light-assisted production of hydrogen. The fundamental aspects of photocatalysis on the most studied photocatalyst, titania (TiO<sub>2</sub>), are still being actively researched and have recently become quite well understood. The mechanisms by which certain types of organic compounds are decomposed completely to carbon dioxide and water have been delineated. However, certain aspects, such as the photo-induced wetting phenomenon, remain controversial, with some groups maintaining that the effect is a simple one in which organic contaminants are decomposed, while other groups maintain that there are additional effects in which the intrinsic surface properties are modified by light. During the past several years, powerful tools such as surface spectroscopic techniques and scanning probe techniques performed on single crystals in ultrahigh vacuum, and ultrafast pulsed laser spectroscopic techniques have been brought to bear on these problems, and new insights have become possible. Quantum chemical calculations have also provided new insights. New materials have recently been developed based on TiO<sub>2</sub>, and the sensitivity to visible light has improved. The new information available is staggering, but we hope to offer an overview of some of the recent highlights, as well as to review some of the origins and indicate some possible new directions.

In this lecture, I will follow the history of TiO<sub>2</sub> photocatalysis, outline the contribution of photocatalysis to a comfortable and safe urban environment, and highlight some important points related to the future development of photocatalysis, including the problem of utilizing visible light and the standardization of photocatalytic systems. I will also introduce our Photocatalysis Museum, which is attached to the Kanagawa Academy of Science and Technology. In addition, I will present some of our recent studies on novel photocatalyst materials and novel applications of photocatalysis.

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## **PC-02      Nutraceuticals and Functional Foods: Their Chemistry and Role in Health Promotion**

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Nutraceuticals and functional food ingredients are important in rendering physiological benefits and reducing the risk of a myriad of degenerative disorders. Therefore, their intended use is for prevention rather than treatment. While nutraceuticals are used in the medicinal form, functional foods resemble commonly used traditional foods. In this connection, there are two classes of compounds that have received increasing attention in recent years. These include antioxidants, represented mainly by phenolic and polyphenolic compounds, and omega-3 oils. Phenolic compounds are secondary metabolites of phenylalanine and tyrosine, and are widely distributed in plants. The health benefits of antioxidants, including phenolic compounds, are rendered by their ability to neutralize free radicals, among others, for relieving oxidative stress and associated disorders. Meanwhile, omega-3 fatty acids, mainly those from the liver of lean fish such as cod and halibut, the body of fatty fish such as salmon, mackerel and herring or blubber of marine mammals such as whales and seals as well as algal sources, are appreciated for their cardioprotective role and anti-inflammatory function. The presentation will provide a cursory account of the chemistry and health promotion and disease risk reduction of these bioactives. It will also provide examples of unexpected results when bioactive compounds are conjugated together, such as green tea catechins with omega-3 fatty acids where the resultant esters played a multifunctional role in disease risk reduction.

## PC-03      The importance of secoiridoid derivatives in food chemistry

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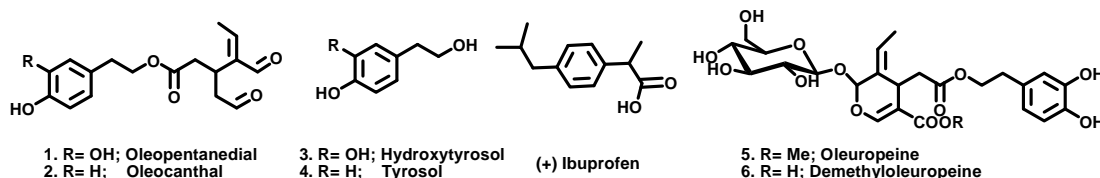
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Oleuropein and its derivatives are secoBiophenols present in considerable amounts in olive leaves, drupes and virgin olive oils, which are responsible for its peculiar bitter taste and its stability.[1] Recent findings demonstrate that olive vegetation water (OVW) is active like a natural anti-inflammatory drug. Moreover, (-) oleocantal, a fenolic aglycone of olive oil responsible for throat irritation, inhibit the cyclooxygenase enzymes in the prostaglandin-biosynthesis pathway with the same potency and profile of ibuprofen.[2]

The easy access to the oleopentadiol,[3] High-Throughput Assayed the UHPLC-ESI-MS/MS and Isotope Dilution Methods,[4] has allowed us also to investigate the the anti-inflammatory effect of oleopentanedial in a cell model we developed to mimic inflammatory injury of endothelium. Another a set of hydroxytyrosol conjugates with fatty acids at different molecular weights was synthesized under mild conditions. The topical delivery features of these new set of antioxidant molecules was evaluated as a function of their permeation profiles through the human stratum corneum and viable epidermis (SCE) membranes.[5]



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## PC-04 Traceability of extra virgin olive oil by tandem mass spectrometry and spectroscopic analyses

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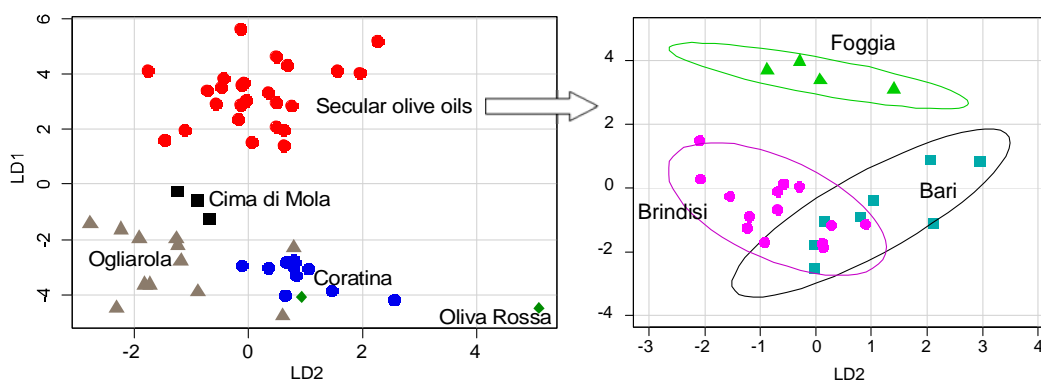
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Recently, the European directives need that the origin of extra virgin olive oils should be clearly stated in the label. Particularly, PDO production is usually confined in a well-determined area and any fraudulent addition of foodstuff produced outside the defined area may alter the quality of the product. The discrimination between olive oils coming from different country, regions and/or area can be afforded by multivariate analysis of analytical data from extra virgin olive oils.

Analytical methods based on ICP-MS and high field NMR spectroscopy allows rapid determination of trace metals and <sup>1</sup>H resonances, respectively. Quantitative <sup>1</sup>H NMR data and ICP-MS data are very suitable to chemometrical analysis.

In general, the determination of metals and trace elements by ICP/MS in olive oil is important because of both the metabolic role of metals, for toxicological reasons and for olive oil traceability [1]. Rapid determination of 18 elements present in olive oil by ICP/MS, allowed, by means of linear discriminant analysis (LDA), the classification of unknown samples after checking possible differentiation of samples of known origin [1].

Apulia region is, traditionally, the most important area for olive oil production in Italy. Nevertheless the wide olive germplasm collection is not completely identified and a number of valuable cultivars are not enrolled yet in the Register of olive cultivation. About 10% of the genetic patrimony is constituted, in particular, of the secular and monumental olive trees. Characterization of extra virgin olive oils obtained from secular olive trees is a key factor to increase the value for this specific production. On the other hand this economic issue is very important to preserve the unique landscape offered by the ancient olive groves of the Apulia region in south east Italy. In this work, a first level investigation was carried out to study the variability and the relatedness inside a sample of secular trees and in comparison with known autochthonous cultivars. Multivariate analysis of <sup>1</sup>H NMR data for microextracted apulian extra virgin olive oils has been successfully used beside other spectroscopic techniques to characterize and differentiate secular from single cultivar genetically certified samples [2]. Moreover, olive oils obtained from secular olive trees could be easily differentiated not only from oils produced outside Italy but also according to their geographical origin within the different districts of the Apulia region.



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## **PC-05      Combined efforts of Apulian institutions, research centers and companies to setup new strategies for valorization of food products: the role of Chemistry**

### **V. Gallo**

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In the foodstuff market, development of valorization strategies of food products represents an “ever green” issue that companies must face. In this framework, chemistry has always helped to preserve the trust between producers and consumers. Continuous efforts to develop powerful analytical methods resulted in excellent levels of quality control in terms of food safety. In fact, before commercialization, producers are obliged to follow strict protocols with the aim to certify, for instance, the absence (or the presence within the allowed limits) of dangerous residues from phytosanitary products. However, quality control in terms of merchandising is still based on declarations of typicality and geographical origin of the food products by producers, without the support of analytical methods. This makes difficult the valorization of food products, especially when producers apply for getting valuable valorization tools such as PDO (Protected Designation of Origin), PGI (Protected Geographical Indication) or TSG (Traditional Speciality Guaranteed) appellations.

Metabonomics aims to measure the global, dynamic metabolic response of the living systems to biological stimuli and represents the appropriate tool to certify quality, typicality and geographical origin of food products. Unfortunately, metabonomics is not yet recognized as a tool for official certifications, mainly because of lack of dialogue between institutions, research centers and companies.

In this communication, some projects launched by SAMER (Special Company of the Chamber of Commerce of Bari) that are aimed to valorize Apulian food products (wine, olive oil and table grapes) will be presented. In particular, two points will be highlighted: 1) the results of cooperation between SAMER, DIAC – Polytechnic of Bari, Innovative Solutions (Spin Off at Polytechnic of Bari) and other partners; 2) the role of Chemistry in the valorization of Apulian table grapes.

## **PC-06      Cultura chimica, scuole, cittadinanza scientifica**

### **Pietro Greco**

Viviamo nell'era della conoscenza ed emerge una nuova domanda di diritti diffusi chiamati diritti di cittadinanza scientifica, il cui presupposto è una diffusa cultura scientifica. La scuola è uno dei luoghi privilegiati per la diffusione di questa cultura.

Della cultura scientifica di base necessaria nell'era della conoscenza è parte imprescindibile la cultura chimica. Luoghi critici di diffusione della cultura chimica sono la scuola e i mass media.

La scuola non sempre riesce a trasmettere le nozioni e i concetti chimici di base che tutti devono possedere; la specifica identità culturale della chimica; il ruolo della chimica nello spazio delle scienze. Anche sui mezzi di comunicazione di massa l'immagine della chimica continua a essere distorta.

I chimici devono impegnarsi in maniera più sistematica per la diffusione di una solida cultura chimica nell'ambito della costruzione di una matura cittadinanza scientifica.



## PC-07      **Dynamic Covalent Capture: Dynamic Chemistry for Biomolecular Recognition and Catalysis**

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Catalyst development is a challenging task, caused by the subtle effects that determine whether a catalyst is efficient or not. The chance of success is enhanced by using methodology that relies to a smaller extent on rational design.[1] The use of dynamic or reversible chemistry for the construction of catalysts is an attractive option as it allows for self-assembly and self-selection processes by the target.[2] Synthesis is restricted to the building blocks after which diversity is simply generated upon mixing.

Our initial challenge was to develop methodology that allows small differences in binding energy to be detected accurately. Recently, we have started to use a dynamic covalent capture approach in which intramolecular interactions affect the thermodynamic landscape of a dynamic combinatorial chemistry.[3] Because relying on the occurrence of intramolecular interactions, the dynamic covalent capture approach has a high sensitivity and is able to detect weak interactions that would go unnoticed otherwise. We have shown that this allows for the self-selection of functional groups able to assist intramolecularly in the cleavage of a neighbouring carboxylic ester.[4]

Currently, we are increasing the complexity of the system by assembling catalytic units on the surface of monolayer protected Au nanoparticles (Au MPCs).[5,6] It will be shown that the assembly of small peptides on the surface of a Au MPC causes a strong increase in catalytic activity.

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## PC-08 MOSAIC: Patterning the surface of monolayer-protected nanoparticles to obtain intelligent nanodevices

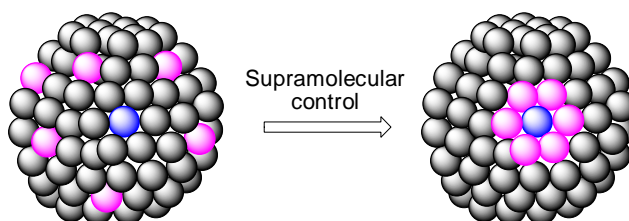
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The concept of “molecular machines” has become common even in the everyday language to describe the ultimate achievements expected from chemical research. The term has gained a much broader significance than the original one and includes any molecular or nanoscopic entity capable to perform the highly sophisticated functions typical of macroscopic devices, ranging from controlled dislocation to transformation, delivery and information processing.

While chemical science is still striving in the search for such molecular machinery, real and perfectly working molecular machines have been developed millions of years ago by Nature. When the main characters at play in biological systems, such as proteins, nucleic acids, and membranes, are examined in detail, one striking feature that emerges is their intrinsic functional simplicity, since only a few building blocks are used to build complex structures. Apparently, what matters is not chemical complexity but the ability of precisely control the spatial arrangement and organization of simple building blocks.

Functional nanoparticles, where a metal nanocluster is stabilized by a monolayer of organic molecules, offer unmatched opportunity to build complex structures with simple building blocks and relatively simple manipulations. The main goal of the Mosaic project is to gain the ability to hierarchically control the self-assembling of metal nanoparticles coating monolayers and take advantage from such ability to obtain complex function from the materials realized. This objective will require to reach a complete understanding of the structure and dynamic of nanoparticles coating monolayers developing new tools for their investigation. Then, we plan to learn how to use supramolecular interactions to control the monolayer organization and to gain, in this way, the ability to program functional groups patterns on the surface of the particles. In this way, it will be possible to achieve a degree of organization comparable to that of biologic systems, such as enzymes or membranes. This organization of functional groups will be then used to obtain highly sophisticated function by these nanosystems, such as recognition, sensing, catalysis and transport. Supported by the ERC Starting Grants Project MOSAIC (grant 259014).



## **PC-09      Electronic Structure of Chemical and Biochemical Systems: Multiscale Approach with Electron Correlation**

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The currently available computational methods have often serious limitations to treat systems where electron correlation plays an important role. Many issues concerning the electronic structure of radicals, photoreceptors and near-half-filled transition metals (Cr,Mo,Fe,Ni) are of paramount relevance in basic and applied research in Chemistry and Biochemistry, but still out of the capabilities of standard and conventional tools such as Density Functional Theory (DFT). On the other hand, the application of more computationally demanding post-Hartree-Fock methods are currently limited to few atoms. The objective of the European Research Council project MultiscaleChemBio (Grant n° 240624) is to overcome these limitations and to develop and apply an innovative and unconventional computer simulation technique to unravel the electronic properties of strongly correlated chemical and biochemical systems. The methodology is based on a multiscale approach based on Quantum Monte Carlo (QMC), DFT and Molecular Mechanics. In term of scaling of the computer time as a function of the system size  $N$ , the proposed approach has a better behaviour than others standard quantum chemistry methods of equivalent level ( $\sim N^4$  vs  $\sim N^7$ ). The multiscale technique is under development and it will be used to address challenging open problems in the chemistry and biochemistry of radical compounds, photoreceptors, transition metal catalysis and enzymatic activity. One important part of the applications will be devoted to the study of the molecular mechanisms regulating natural and artificial photosynthesis.

## **PC-10      New functionalized nanoparticles as MRI and molecular imaging contrast agents: chemical, physical and relaxation properties.**

### **V. Domenici**

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In this presentation, I will talk about the project “*Caratterizzazione chimico fisica di nuovi agenti di contrasto per risonanza magnetica di imaging (MRI) a 7 Tesla*”, granted by L’Oreal Italia-Unesco in 2010. In particular, the focus is on functionalized iron oxide nanoparticles, deeply investigated in the last years for their high potentialities for biomedical applications, both diagnostic and therapeutic ones [1,2]. The efficiency of these nanoparticles as MRI contrast agents and in particular their effect on the  $^1\text{H}$  relaxation rates,  $R$  ( $\text{s}^{-1}$ ), of water molecules is related to a complex interplay [3] among different features, such as magnetic-core size, monodispersivity, type of coating, concentration in water, magnetic field strength and cluster formation [4].

#### *Acknowledgments:*

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## **PC-11      ‘Vincenzo Caglioti’ Prize and Computational Chemistry**

### **A. Pedone**

The computational simulation of matter at the atomic level is now an essential tool for contemporary science. Atomic modeling techniques are used routinely in the study of proteins and pharmaceuticals and in the conformational analysis of organic molecules. Computational methodologies have, however, an equally important role in the study of inorganic and hybrid materials.

My research activity, which started in 2005, is focused on the calculation of chemical-physical properties of complex systems such as silica-based glasses, biomaterials and dye-doped silica nanoparticles.

In this communication, a brief discussion on the potentialities reached by computational chemistry to the study of real systems will be offered by taking some examples from my previous works which allowed me to win the prestigious prize released by the ‘Accademia Nazionale dei Lincei’.

The final aim is to demonstrate that computational chemistry is now an essential tool to guide and support experimental studies and succeed in ambitious Italian and European research projects.

## **PC-12      Molecular/Hybrid      Micro-Nanotechnologies      for      Photonic Applications**

**Giuseppe Gigli**

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Despite the growing interest in organic and hybrid materials based on colloidal nanocrystals, related to their excellent properties in terms of colour tuning, flexibility and low cost of fabrication, the persisting limit for their full exploitation in advanced devices stands in the lack of well established lithographic and device fabrication techniques suitable for this class of materials. Conventional lithographic technologies, such as photolithography and electron beam lithography, are not in fact compatible with soft and soluble molecular materials and standard deposition techniques are not suitable for novel hybrid nanocomposites. This prevents the possibility to realize complex devices and nanostructures able to increase device performances. Thus, a step forward for organic/hybrid opto-electronics necessarily passes through the development of a suitable technology for high resolution patterning and material deposition. In this talk novel approaches for the fabrication of advanced organic and hybrid photonic devices , such as lasers, light emitting diodes, emitting fibers and solar cells will be presented.

## **PC-13      Application of Semiconductor Nanomaterials in Solar Energy Conversion Processes**

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The contribution will focus on the use of semiconductor nanomaterials for direct conversion of solar energy to electricity in Dye Sensitized Solar Cells (DSSCs) as well as in photoinduced water splitting processes.

DSSCs are among the most promising solar energy conversion devices of new generation, since they may couple ease of fabrication, low cost and offer the possibility of building integration in photovoltaic windows and facades. Although in their earliest configuration these systems are close to commercialization, fundamental studies are still required for developing new molecules and materials with more desirable properties. Some recent advances made in the effort of improving DSSCs efficiencies by finding alternative materials are presented.

In the field of hydrogen production, it has recently been found that potentiostatic anodization of metallic tungsten in a suitable solvent provides an effective mean for producing a highly efficient nanostructured WO<sub>3</sub> layer for photoassisted electrolysis. Under 0.3 W/cm<sup>2</sup> solar irradiation, plateau photocurrents in the order of 10 mA/cm<sup>2</sup> are reproducibly observed in acidic medium.

Recent advances in the field of photoelectrochemical (PEC) cells applied to water and H<sub>2</sub>S splitting are also discussed.

## **PC-14 Con le Nanotecnologie copiamo la Natura: Biomimetismo e Geomimetismo.**

**"La Natura, il supremo architetto da cui imparare a costruire i materiali del domani"**

**N. Roveri**

Chiamiamo “materiali biogenici”, i materiali prodotti dai sistemi biologici, ovvero i materiali di cui sono costituiti gli esseri viventi che popolano il nostro pianeta, siano essi vertebrati o invertebrati, esseri umani o unicellulari. I materiali biogenici sono costituiti da un limitato numero di molecole e composti chimici che la Natura utilizza per ottenere materiali con proprietà e funzionalità molto diverse tra loro. I materiali biogenici presentano un elevato grado di sofisticazione strutturale, miniaturizzazione, organizzazione gerarchica, efficienza, resistenza alla fatica, capacità autoriparative ed adattabilità ai cambiamenti dell’ intorno. Tutte proprietà che i materiali biogenici hanno acquisito attraverso specifici meccanismi di formazione selezionati dall’ evoluzione che possono essere ottenute solo molto parzialmente nei materiali che noi prepariamo con gli attuali processi di sintesi. Per questa ragione la Natura è una importante scuola e fonte di ispirazione per chi si occupa di scienza dei materiali e il biomimetismo rappresenta una guida importante per la progettazione e la sintesi di materiali innovativi e tecnologici.

Mimando la Natura noi possiamo progettare e sintetizzare nuovi materiali sia inorganici che macromolecolari che vengono definiti “intelligenti” perché sono reattivi con i tessuti biologici e stimolano specifiche reazioni cellulari. Il biomimetismo dei materiali sintetici può essere portato avanti a vari livelli: composizione chimica, struttura, morfologia, area e reattività superficiale, aggregazione delle unità nanometriche fino a livello macroscopico cercando di mimare il più possibile i materiali biogenici. La chimica oggi grazie alle nanotecnologie e alle biotecnologie può spingere il biomimetismo fino a mimare le condizioni dei processi biochimici naturali utilizzando processi sintetici in base acquosa senza l’ utilizzo di solventi organici, utilizzando soluzioni diluite e condizioni sintetiche a bassa pressione e temperatura. La chimica biomimetica non perturba l’ ambiente e riesce a produrre materiali sintetici che le cellule scambiano per biogenici e come tali li accettano e li utilizzano.

Il biomimetismo si accompagna al geomimetismo il quale mima i materiali naturali di origine geologica quando questi presentano delle proprietà chimiche e strutturali che li rendono interessanti per specifiche applicazioni. L’esempio, io credo, più eclatante è quello delle fibre minerali di amianto che hanno rappresentato, rappresentano e continueranno a rappresentare uno dei pericoli più terrificanti per la salute umana. L’ utilizzo delle fibre di amianto nel preparare manufatti industriali ha rappresentato un tragico errore del passato, ma la sintesi geomimetica di fibre di amianto sta rappresentando una prospettiva tecnologica del futuro. Infatti fibre che mimano per composizione, struttura e morfologia le fibre di amianto possono essere sintetizzate in laboratorio senza la presenza di certi ioni metallici che rendevano tossiche e cancerogene le fibre minerali. Non solo queste fibre sintetiche di amianto geomimetico non risultano tossiche e pericolose per la salute umana, ma rappresentano un innovativo materiale nanostrutturato a morfologia tubolare che potrà in futuro essere utilizzato per innovative applicazioni tecnologiche come nella realizzazione di nuovi pannelli fotovoltaici e pile per un più efficiente utilizzo dell’ energia solare.



## **PC-15      Multiscale Simulations of Membrane Proteins**

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Membrane proteins account for 25% of genes. They perform a number of key functions in cells, including transport and signalling across membranes. Advances in structural biology will reveal ca. 2500 structures for membrane proteins by 2020. However, experimental structures of isolated membrane proteins do not reveal their interactions with lipid bilayers or with other proteins in membranes. Multiscale MD simulations, by combining coarse-grained and atomistic resolution [1], allow us to probe the interactions of membrane proteins with their lipid bilayer environment. I will discuss the use of such simulations to probe protein/lipid and protein/protein interactions in membranes. I will illustrate this discussion with examples of recent studies of such interactions, including recognition of cell membranes by lipid binding PH domains [2], and signalling across cell membranes by integrins [3].

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## PC-16      **Ingegneria inversa delle idrogenasi: il contributo degli studi QM e QM/MM.**

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Con il nome di ingegneria inversa vengono convenzionalmente indicati quei processi che permettono di rivelare i principi alla base del funzionamento di un dispositivo, mediante l'analisi della sua struttura, della sua funzione e del suo modo di operare. Dal punto di vista operativo, l'ingegneria inversa solitamente prevede l'analisi delle componenti di un dispositivo, al fine di progettare un dispositivo caratterizzato da analoghe funzioni.

Anche se il termine ingegneria inversa si applica generalmente allo studio di dispositivi progettati dall'uomo, la sua logica e le sue operazioni sono altrettanto efficaci nello studio di dispositivi molecolari (quali ad esempio gli enzimi) che sono stati plasmati e ottimizzati in milioni di anni di selezione naturale.

In particolare, l'ingegneria inversa applicata agli enzimi prevede generalmente i seguenti passaggi: a) identificazione della funzione dell'enzima, b) caratterizzazione strutturale, c) caratterizzazione del modo in cui opera il dispositivo molecolare (cioè descrizione del meccanismo catalitico), d) valutazione del ruolo di specifiche componenti dell'enzima sul modo di operare, e) progettazione di dispositivi molecolari originali utilizzando i principi acquisiti studiando il dispositivo originale.

Le idrogenasi sono enzimi che catalizzano la trasformazione di protoni ed elettroni in idrogeno molecolare, e rappresentano un esempio particolarmente interessante di dispositivi molecolari di origine naturale su cui si possono applicare i metodi dell'ingegneria inversa [1-3]. In particolare, tra i vari strumenti a disposizione del chimico, i metodi quantomeccanici si sono rivelati particolarmente efficaci in tutti gli stadi del processo di ingegneria inversa delle idrogenasi. In questo contributo verranno presentati recenti risultati riguardanti le proprietà elettroniche e strutturali di [FeFe] idrogenasi in differenti stati redox e di protonazione, e verrà discussa la loro rilevanza nella progettazione razionale di nuovi catalizzatori sintetici [4-7].

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## **PC-17 Probing the link between target affinity, ADMET and physicochemical properties: use of the “drug efficiency index” in modern drug discovery**

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One of the key goals of drug discovery is to develop new medicines with low therapeutic dose to reduce drug burden and so to limit the attrition for direct organ toxicity. In order to achieve this, a common strategy is to maximize the target affinity under the assumption that only highly potent compounds have greater potential to translate into successful, low-dose therapeutics. This has led to the development of screening cascades with in vitro potency embedded as an early filter. However, this approach is beginning to be questioned, given the bias in structural properties that it can introduce early in lead generation and optimization. This bias is due to the often diametrically opposed relationship between physicochemical parameters associated with high in vitro potency and those associated with desirable absorption, distribution, metabolism, excretion and toxicity (ADMET) characteristics.

This lecture emphasizes the need to link early on in the process structural and biological design considering mathematically relevant equations for the prediction of drug efficacy. The drug efficiency index (DEI) is introduced as a single parameter directly connected to therapeutic dose with the potential to help lead optimization towards the selection of superior clinical candidates.

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## PC-18      The Future of Fossils

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The today total primary energy supply is 112300 Mtoe<sup>1</sup>; the fossil fuels cover a little more than 80% of the total. The request of energy is expected to growth substantially in the next two decades. The percentage may range from 35% to 20% depending of the scenario adopted: the highest connects with the Reference Scenario, where the business continues as usual, and the lowest connects with the Alternative Policy Scenario (known as 450\_Policy Scenario) where governments are adopting energy policies favouring a low carbon economy to reduce the GHG concentration in the atmosphere. Even in the latter scenario, however, the fossil fuels will cover about 70% of the energy mix in the year 2030.

Today the proved reserves of oil, gas and carbon amounts respectively to 1191 billion of barrels<sup>2</sup>, 193,117 billion cubic meters<sup>2</sup> and over 847 billion tonnes<sup>3</sup>. This means that the life index, i.e. how many years a resource is expected to last of the current rates of production, are respectively 40 years for oil, 60 for gas and 118 for coal.

Earth hides more fossil fuels, often referred to as “unconventional” for oil and gas, that can easily double the amount of fossil energy available per source. Even more some of them are already tapping the world energy scenario: the shale gas is today booming particularly in the USA, allowing them to export gas while until a few years ago they were net importers.

Coal reserves to production ratio instead has been falling in the past years, probably because the use has grown quite rapidly (pushed by the large use of India and China as a very cheap primary source) and because a lack of incentives to promote the discovery of new reserves. The general conviction is that new discoveries are possible and the potential of developing countries are partially unknown.

The presentation discusses how the fossil fuels can constitute the back bone of the world energy system in the transition toward a carbon free energy

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The aim of this contribution is to provide an overview of the state of the art on the CO<sub>2</sub> capture technologies with a mention on Enel CCS project.

CCS (Carbon Capture and Storage) technologies are seen as an important option for the climate change strategy in order to control the CO<sub>2</sub> emissions. Post-combustion CO<sub>2</sub> capture with amines technology is considered the most mature technology for medium term industrial application because i) experience on CO<sub>2</sub> capture (up to 300 TPD) by means of chemical absorption processes had been developed for CO<sub>2</sub> separation in Oil and Gas and chemical industry; ii) amine-base processes have been already tested at pilot.

One of the main research issues in the field of amine based solvent is finding the optimal solvent components: sterically hindered amines, ionic liquids, amino acids.

Moreover several alternative approach are under investigation: solid sorbent, membranes, enzyme based solvents, etc.

## PC-20      Towards a CO<sub>2</sub>-H<sub>2</sub> economy?

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The urgent need for strategies to develop new methodologies which allow to move towards a cleaner energy system has prompted actions from national and international governments and industries, and a number of high-profile collaborative programs have been established (Intergovernmental Panel on Climate Change, United Nations Framework Commission on Climate Change, and Global Climate Change Initiative). The first step to change our energy system seem to be the reduction of CO<sub>2</sub> emission which requires new technologies able to reduce the CO<sub>2</sub> emission. Besides the well established CCS (Carbon Capture and Storage) technology a CCU (Carbon Capture and Utilisation) approach may play a major role: Carbon dioxide may represent an interesting raw material for developing innovative synthetic methodologies less intensive in carbon and energy. It can be used as building block for the synthesis of other C1 molecules, such as formic acid and methanol, and molecular and polymeric chemicals or source of carbon for fuels.

Concurrently, much attention is paid to the production and use of dihydrogen which rises concerns for its storage and transportation.

Then, why not to merge the two issues above and implement an operative solution for the conversion of large volumes of CO<sub>2</sub> by its hydrogenation into liquid fuels or methane?

Two possible approaches will be discussed: (i) the preliminary production of dihydrogen from renewable sources and water; (ii) the direct reduction of CO<sub>2</sub> in water.

The actual barriers to a large scale exploitation will be highlighted.

## **PC-21      The Central Role of Catalysis in Next Generation Biorefineries**

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The development and implementation of biorefinery processes is of the utmost importance to meet the vision towards a sustainable economy based on bio-resources. In this context, catalysis, either enzymatic, heterogeneous or homogeneous is playing a major role like this is already the case in a 'conventional' refinery based on the treatment and the conversion of petro-resources. Nevertheless, contrary to petro-resources of which the nature and composition variations are 'relatively' limited, under the term 'bio-resource' or 'biomass' are gathered compounds of very different natures, namely cellulose, hemicellulose, oils, lignin and so on... Thus, a complete set of specific technologies must be developed in order to convert each fraction as smartly as possible. This implies, among others, the elaboration of a lot of processes based on catalysis. These latter constitute core technologies that will be implemented in the so-called 'biorefineries'. Within this frame, we are coordinating the elaboration and the development of the EuroBioRef concept 'EUROpean multilevel integrated BIOREFinery design for sustainable biomass processing', as a 'large-scale' European project. EuroBioRef is a new highly integrated, diversified and sustainable concept, which involves all the biomass sector stakeholders. The potential of all the fractions issued from the various types of biomass is used to yield a value-added as high as possible in a sustainable and economical way. The overall efficiency of this approach will be a vast improvement to the existing situation and considers options such as: Production and use of a high diversity of sustainable biomass adapted for European regions / Production and use of high specific energy bio-aviation fuels (42 MJ/kg) / Production of multiple products (chemicals, polymers, materials) in a flexible and optimized way that takes advantage of the differences in biomass components and intermediates / Improvement of the cost efficiency by as much as 30 per cent through improved reaction and separation effectiveness, reduced capital investments, improved plant and feedstock flexibility and reduction of production time and logistics / Reduction by 30 per cent of the required energy / Zero waste production and reduction of feedstock consumption. The EuroBioRef novel concept will be presented, in which the central and key role of catalysis will be discussed.

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## PC-22 Perspectives in Chemistry: From Supramolecular Chemistry towards Adaptive Chemistry

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Supramolecular chemistry is actively exploring systems undergoing *self-organization*, i.e. systems capable of spontaneously generating well-defined functional supramolecular architectures by self-assembly from their components, on the basis of the *molecular information* stored in the covalent framework of the components and read out at the supramolecular level through specific non-covalent interactional algorithms, thus behaving as *programmed chemical systems*.

The design of molecular information controlled, “programmed” and functional self-organizing systems provides an original approach to nanoscience and nanotechnology. The spontaneous but controlled generation of well-defined, functional molecular and supramolecular architectures of nanometric size through self-organization represents a means of performing programmed *engineering* and *processing* of *functional nanostructures*. It offers a very powerful alternative to nanofabrication and to nanomanipulation for the development of nanotechnology.

Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their components. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibly, so as to allow a continuous change in constitution by reorganization and exchange of building blocks. These features define a *Constitutional Dynamic Chemistry* (CDC) on both the molecular and supramolecular levels.

CDC introduces a paradigm shift with respect to constitutionally static chemistry. The latter relies on design for the generation of a target entity, whereas CDC takes advantage of dynamic diversity to allow variation and selection. The implementation of selection in chemistry introduces a fundamental change in outlook. Whereas *self-organization by design* strives to achieve full control over the output molecular or supramolecular entity by explicit programming, *self-organization with selection* operates on dynamic constitutional diversity in response to either internal or external factors to achieve *adaptation*.

Applications of this approach in biological systems as well as in materials science will be described.

The merging of the features: - information and programmability, - dynamics and structural diversity, -constitution and selection, points towards the emergence of *adaptive* and *evolutive chemistry*.

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## **PC-23      Exploring the Protein Universe with Physical Chemistry Tools**

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Structural biology is a highly attractive area for applications of methods of physical chemistry. For example, my research team is specialized in the use of nuclear magnetic resonance (NMR) spectroscopy for studies of proteins and other biological macromolecules. Thereby, NMR studies in classical “structural biology” are focused on proteins of well-known biological or biomedical interest, with examples from my laboratory in the areas of oxygen transport, immune suppression, differentiation in higher organisms, and transmissible encephalopathies such as mad cow disease. In today’s post-genomic era, with the availability of the complete DNA sequences of a wide range of organisms, we are additionally faced with new opportunities and challenges in “structural genomics”. The focus is then on gene products with unknown structures, unknown functions, and minimal similarity to previously studied proteins, in order to increase coverage of the protein sequence universe with three-dimensional structures. My team participates in projects of the Protein Structure Initiative (PSI:Biology, [www.jcsg.org/prod/newscripsts/sg-centers.cgi](http://www.jcsg.org/prod/newscripsts/sg-centers.cgi)) and the NIH Roadmap for Medical Research (<http://commonfund.nih.gov/aboutroadmap.aspx>) which use another method of physical chemistry, structure determination by X-ray crystallography, as the principal technique. This presentation describes our strategies for use of solution NMR spectroscopy with soluble and membrane proteins in these crystallography-centered environments. Our approaches should ensure an exciting role for NMR in the longer-term challenge leading from the expanding protein structure universe to new insights into protein functions and chemical biology, by generating data on protein structure, conformational equilibria, dynamics and intermolecular interactions in solution.